Numerical Estimation in a Theory of Interfacial Polarization Developed for Disperse Systems in Higher Concentrations

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 54, No. 4, 1976

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Received June 16, 1976

Numerical calculations are carried out to obtain solutions of a theoretical expression of interfacial polarization, which was proposed by Hanai [*Kolloid Z.*, **171**, 23 (1960)], applicable to concentrated disperse systems of spherical particles. It is found that the dielectric relaxation characterized by the changes in the dielectric constants and the electrical conductivities extends over an apparently broader range of frequency in comparison with a single relaxation system, and that the complex plane plots of the complex dielectric constants show remarkable depression from a semicircle. Some comparisons of the limiting dielectric constants and electrical conductivities at low and high frequencies are made between the present results and those by approximate equations so far used. The relaxation frequency giving the maximum loss factor is found to be strongly dependent on the concentration of the disperse phase and to reduce to very low values at higher concentrations in conformity with experimental results.

I INTRODUCTION

As is well known, a heterogeneous system of spherical particles dispersed in a continuous phase shows a dielectric relaxation due to interfacial polarization. The dielectric relaxation has been discussed by many workers[1] qualitatively in the light of Wagner's theory. Since closer consideration revealed that Wagner's theory was in agreement with experimental results only at lower concentrations of the disperse phase, Hanai[2,3] proposed a theory which is expected to be applicable to higher concentrations.

According to our dielectric study of water-in-oil (W/O) emulsions,[4,5] remarkable dielectric relaxations were observed in accordance with Hanai's theory, and the limiting dielectric constants at high frequencies showed excellent agreements with the theory. In our previous work on the dielectric relaxations of W/O emulsions,[5] the limiting dielectric constants at low frequencies were also in good agreements with the theory as far as the W/O emulsions are prepared by minimal use of emulsifiers.

The expression of this theory is of a functional form including a cubic root of complex variable, and is impossible to be rearranged so that the relaxation frequency may be numerically calculated. Hence the comparison was not made between the theoretical and the experimental values.

Clausse[6,7,8,9] performed computer analyses of this theoretical expression for the purpose of discussing his data on emulsions. Nevertheless it is still necessary for the discussion of our experimental data to estimate the results by using our measured values on the constituent phases.

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In the present paper, the expression of Hanai's theory is calculated by means of a programmable calculator, giving the frequency dependence of the dielectric constants, the electrical conductivities, and the loss factors. The limiting dielectric constants and the electrical conductivities at low and high frequencies and the relaxation frequencies are evaluated as well, and are compared with those from approximate formulas and experimental values.

II GLOSSARY OF SYMBOLS

ε_a dielectric constant of the continuous medium.
κ_a electrical conductivity of the continuous medium, S cm^{-1}.
ε_i dielectric constant of the disperse phase.
κ_i electrical conductivity of the disperse phase, S cm^{-1}.
ε dielectric constant of the disperse system.
κ electrical conductivity of the disperse system, S cm^{-1}.
ε_a^*, ε_i^* and ε^* are complex dielectric constant of the continuous medium, the disperse phase and the disperse system respectively, being given by

$$\varepsilon_a^* = \varepsilon_a - j\frac{\kappa_a}{2\pi f\epsilon_v}, \tag{1}$$

$$\varepsilon_i^* = \varepsilon_i - j\frac{\kappa_i}{2\pi f\epsilon_v}, \tag{2}$$

and

$$\varepsilon^* = \varepsilon - j\frac{\kappa}{2\pi f\epsilon_v}. \tag{3}$$

f measuring frequency, Hz.
j unit imaginary, $\sqrt{-1}$.
ϵ_v dielectric constant of free space given by

$$\frac{1}{4\pi\cdot 9\cdot 10^{11}} = 8.8542\times 10^{-14} \text{ F cm}^{-1}.$$

Φ volume fraction of the disperse phase.
ε_l limiting dielectric constant at low frequencies.
κ_l limiting conductivity at low frequencies, S cm^{-1}.
ε_h limiting dielectric constant at high frequencies.
κ_h limiting conductivity at high frequencies, S cm^{-1}.
f_0 relaxation frequency giving the maximum loss factor, Hz.

III COMPUTER EXPERIMENTS ON NUMERICAL CALCULATIONS OF HANAI'S EQUATION

For a complex dielectric constant of a disperse system in which spherical particles are dispersed in a continuous medium by a volume fraction Φ, Hanai[2,3] derived the following equation

$$\frac{1}{1-\Phi}\,\frac{\varepsilon^*-\varepsilon_i^*}{\varepsilon_a^*-\varepsilon_i^*}\left(\frac{\varepsilon_a^*}{\varepsilon^*}\right)^{1/3}=1. \tag{4}$$

By cubing the both sides of Eq. (4), we have the cubic equation with respect to ε^* as

$$\varepsilon^{*3}-3\varepsilon_i^*\varepsilon^{*2}+\left\{3\varepsilon_i^{*2}+\frac{[(\Phi-1)(\varepsilon_a^*-\varepsilon_i^*)]^3}{\varepsilon_a^*}\right\}\varepsilon^*-\varepsilon_i^{*3}=0. \tag{5}$$

Numerical evaluation of the solution was carried out by a calculator, Yokogawa-Hewlett-Packard Model 10, with a programming of the following steps.

(a) Substitution of numerical values of ε_a, κ_a, ε_i, κ_i, and an arbitrary value of f into Eqs. (1) and (2) gives values of ε_a^* and ε_i^*.

(b) The coefficients of the cubic Eq. (5) can be determined by substituting ε_a^*, ε_i^*, and an arbitrary value of Φ.

(c) By the use of a computer programme "Roots of Polynomial with Complex Numbers" (Model 10, MATH PAC III-3), we obtain three roots of Eq. (5) designated by ε_1^*, ε_2^*, and ε_3^*.

(d) Among the three roots ε_1^*, ε_2^*, and ε_3^*, we have to choose only one solution satisfying Eq. (4) by means of the following criterion. Since Eq. (5) is derived by cubing Eq. (4), respective substitution of the three roots ε_1^*, ε_2^*, and ε_3^* into a function

$$F(\varepsilon^*)=\frac{1}{1-\Phi}\,\frac{\varepsilon^*-\varepsilon_i^*}{\varepsilon_a^*-\varepsilon_i^*}\left(\frac{\varepsilon_a^*}{\varepsilon^*}\right)^{1/3} \tag{6}$$

is to give

$$F(\varepsilon_1^*)=1+0\cdot j=e^{j\cdot 0} \tag{7}$$

$$F(\varepsilon_2^*)=-\frac{1}{2}+\frac{\sqrt{3}}{2}j=e^{j\left(\frac{2\pi}{3}\right)} \tag{8}$$

and

$$F(\varepsilon_3^*)=-\frac{1}{2}-\frac{\sqrt{3}}{2}j=e^{j\left(-\frac{2\pi}{3}\right)} \tag{9}$$

respectively. When each of the three roots is thus substituted into $F(\varepsilon^*)$ given by Eq. (6), the roots which lead to either Eq. (8) or Eq. (9) should be ruled out, and only one root giving Eq. (7) adopted as the solution of Eq. (4).

(e) The root is regarded as ε^* of Eq. (3), giving the values of ε, κ, and ε'' for the disperse system.

IV RESULTS

In our previous measurements on W/O emulsions,[5] remarkable dielectric relaxations were observed, and the relaxation frequencies were reported without comparison with those by Eq. (4). Hence, in the present work, the frequency profile of the complex dielectric constant was calculated by using numerical values of ε_a, κ_a, ε_i, and κ_i reported in the previous paper.[5]

The results calculated for $\Phi=0.8$ are shown in Figs. 1 and 2. For comparison, theoretical curves of a single relaxation system, the so-called dielectric relaxation in the Debye type, are shown with dashed curves in Figs. 1 and 2. The decrease in ε and the increase in κ with increasing frequency for Eq. (4) are seen to extend over an apparently

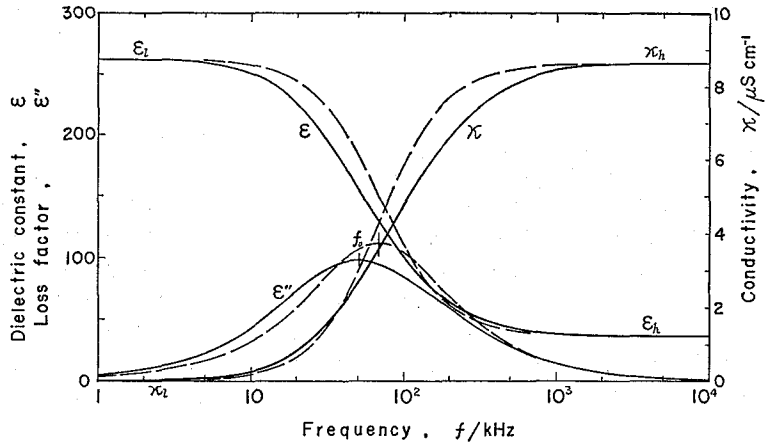

Fig. 1. Comparison of the frequency dependence of dielectric constant ε, electrical conductivity κ, and loss factor ε''. The solid curves are calculated from Equation (4) with volume fraction $\Phi=0.8$ and values of phase parameters shown in Table I. The dashed curves indicate a single relaxation system with the same values of ε_l, ε_h, κ_l, and κ_h as those calculated from Equation (4). As regards the loss factor, curves of $\varepsilon''=(\kappa-\kappa_l)/2\pi f\epsilon_v$ are depicted in the figure.

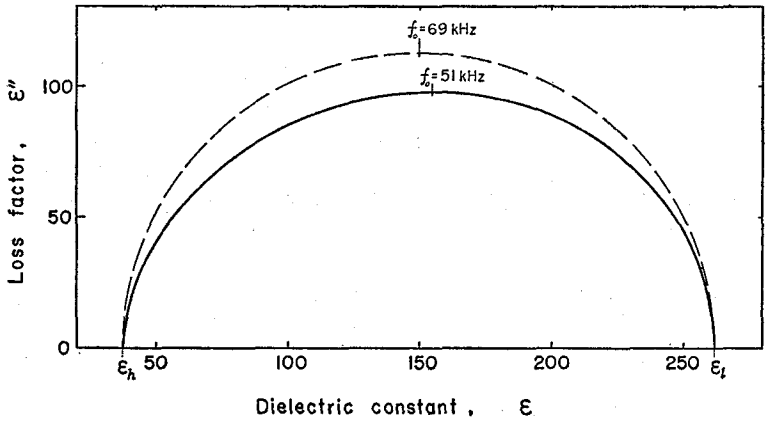

Fig. 2. Complex plane plots of the dielectric constants and the loss factors. The solid curve is given by Equation (4), the dashed curve (semicircle) by a single relaxation system. The same data as shown in Fig. 1.

broader range of frequency in comparison with a single relaxation system, being simulated by system with some distribution of relaxation times. The frequency profile of the loss factor ε'' $(=(\kappa-\kappa_l)/2\pi f\epsilon_v)$ for Eq. (4) seems to be asymmetric with respect to log (f/f_0).

In Table I are summarized the values of ε_l, ε_h, κ_l, κ_h, and f_0 thus calculated from Eq. (4) for various values of Φ. Since f_0 cannot be evluated at $\Phi=0$ owing to no dielectric relaxation, the value of f_0 at $\Phi=0.0001$ is calculated instead.

Table I. Values of Limiting Dielectric Constants ε_l, ε_h, and Limiting Conductivities κ_l, κ_h at Low and High Frequencies, and Relaxation Frequencies f_0 at Various Volume Fractions Φ

Φ	ε_l	ε_h	κ_l / μScm^{-1}	κ_h / μScm^{-1}	f_0 / kHz	ε_l	κ_l / μScm^{-1}	f_0 / kHz
	by Eq. (4)					by Eq. (18)	by Eq. (19)	by Eq. (20)
0.0	2.1000	2.1000	0.0000655	0.0000655	⋯	2.1000	0.0000655	539.0
0.0001	2.1006	2.1006	0.000065519	0.0000942	539.0	2.1006	0.000065519	539.0
0.1	2.8806	2.8010	0.000089849	0.023125	519.9	2.8806	0.000089848	534.4
0.2	4.1014	3.8262	0.00012792	0.075735	493.0	4.1015	0.00012793	528.8
0.3	6.1222	5.3617	0.00019096	0.19339	454.9	6.1224	0.00019096	521.8
0.4	9.7216	7.7096	0.00030323	0.45394	401.7	9.7222	0.00030324	512.7
0.5	16.798	11.346	0.00052397	1.0210	329.3	16.800	0.00052400	500.5
0.6	32.804	16.973	0.0010233	2.2085	237.5	32.812	0.0010234	483.2
0.7	77.732	25.505	0.0024252	4.5285	136.8	77.777	0.0024259	456.9
0.8	261.97	37.932	0.0081794	8.6398	50.98	262.50	0.0081875	412.0
0.9	2066.8	55.095	0.064981	15.164	7.193	2100.0	0.065500	318.3
0.98	85872	72.587	4.4724	22.398	0.1633	262500	8.1875	113.0
1.0	77.5	77.5	24.5	24.5	⋯	∞	∞	0.0561

Values of the phase parameters used for the calculation are cited from the previous work.[5]
Outer oil phase : Dielectric constant $\varepsilon_a=2.10$, conductivity $\kappa_a=6.55\times10^{-11}$S cm^{-1}
Inner aqueous phase: Dielectric constant $\varepsilon_i=77.5$, conductivity $\kappa_i=24.5\times10^{-6}$S cm^{-1}

V DISCUSSION

Comparison of the Present Values with Those Obtained from Approximate Equations.

In our previous papers[4,5] only the limiting cases at high and low frequencies for Eq. (4) were discussed owing to the difficulty of numerical calculations at arbitrary frequencies, and the following relations were derived from Eq. (4).

Irrespective of the emulsion type, we have, at high frequencies ($f\to\infty$),

$$\frac{\varepsilon_h-\varepsilon_i}{\varepsilon_a-\varepsilon_i}\left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3}=1-\Phi, \tag{10}$$

and

$$\kappa_h\left(\frac{3}{\varepsilon_h-\varepsilon_i}-\frac{1}{\varepsilon_h}\right)=3\left(\frac{\kappa_a-\kappa_i}{\varepsilon_a-\varepsilon_i}+\frac{\kappa_i}{\varepsilon_h-\varepsilon_i}\right)-\frac{\kappa_a}{\varepsilon_a}, \tag{11}$$

and, at low frequencies ($f\to0$).

$$\varepsilon_l\left(\frac{3}{\kappa_l-\kappa_i}-\frac{1}{\kappa_l}\right)=3\left(\frac{\varepsilon_a-\varepsilon_i}{\kappa_a-\kappa_i}+\frac{\varepsilon_i}{\kappa_l-\kappa_i}\right)-\frac{\varepsilon_a}{\kappa_a}, \tag{12}$$

and

$$\frac{\kappa_l-\kappa_i}{\kappa_a-\kappa_i}\left(\frac{\kappa_a}{\kappa_l}\right)^{1/3}=1-\Phi. \tag{13}$$

For the W/O type emulsions ($\kappa_i\gg\kappa_a$), Eqs. (10), (11), (12), and (13) reduce to

$$\frac{\varepsilon_i-\varepsilon_h}{\varepsilon_i-\varepsilon_a}\left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3}=1-\Phi, \tag{14}$$

$$\kappa_h=\kappa_i\frac{3\varepsilon_h(\varepsilon_h-\varepsilon_a)}{(\varepsilon_i+2\varepsilon_h)(\varepsilon_i-\varepsilon_a)}, \tag{15}$$

$$\varepsilon_l=\varepsilon_a\frac{\kappa_l(\kappa_i-\kappa_l)}{\kappa_a(\kappa_i+2\kappa_l)}, \tag{16}$$

and

$$\frac{\kappa_i-\kappa_l}{\kappa_i}\left(\frac{\kappa_a}{\kappa_l}\right)^{1/3}=1-\Phi. \tag{17}$$

If it is allowed, further, to put $\kappa_i\gg\kappa_l$, Eqs. (16) and (17) reduce to

$$\varepsilon_l=\varepsilon_a\frac{1}{(1-\Phi)^3}, \tag{18}$$

and

$$\kappa_l=\kappa_a\frac{1}{(1-\Phi)^3}. \tag{19}$$

In our previous papers,[4,5] Eqs. (14), (15), (18), and (19) were eventually used for comparison between theories and experiments.

In order to examine the accuracy of the approximation, the values of ε_h, κ_h, ε_l, and κ_l are calculated from the equations shown above. It is found that the values of ε_h, κ_h, ε_l, and κ_l calculated from Eqs. (10), (11), (12), and (13) are in perfect agreements with those from Eq. (4) listed in Table I.

As regards the approximate equations for $\kappa_i\gg\kappa_a$, the values of κ_h from Eq. (15) are in good agreements with those from Eq. (4) at higher values of Φ, and show smaller values by about 0.1% than those of Eq. (4) at less than $\Phi=0.3$, such differences being insignificant in practice. The values of ε_l from Eq. (16) are in good agreements with those from Eq. (4) in a whole range of Φ.

The approximate equations (18) and (19) simplified by the condition $\kappa_i\gg\kappa_l$ show appreciable deviation from Eq. (4), the calculated values being listed in Table I. The values of ε_l and κ_l by Eqs. (18) and (19) show the differences of more than 1% from those by Eq. (4) at $\Phi=0.9$.

Comparison of the Relaxation Frequency

Most interesting is the profile of the concentration dependence of f_0 values, which are shown in Table I. For comparison, the values from Wagner's expression given by

$$f_0=\frac{\kappa_i+2\kappa_a-\Phi(\kappa_i-\kappa_a)}{\varepsilon_i+2\varepsilon_a-\Phi(\varepsilon_i-\varepsilon_a)}\frac{1}{2\pi\epsilon_v} \tag{20}$$

are also shown in Table I.

Figure 3 shows theoretical curves for the concentration dependence of f_0. At lower concentrations, the curve by Eq. (4) is very close to that by Wagner's theory, whereas at higher concentrations the curve by Eq. (4) shows much lower values than that by Wagner's theory. In Fig. 3 are shown the observed data,[5] which showed the remarkable dependence on the concentration similar to the tendency shown by Eq. (4). It is thus concluded that the concentration dependence of f_0 by Eq. (4) explains the experimental results fairly well. It is desired that values of κ_i is controlled experimentally by the use of salt solutions in definite concentrations to obtain more reliable values of f_0.

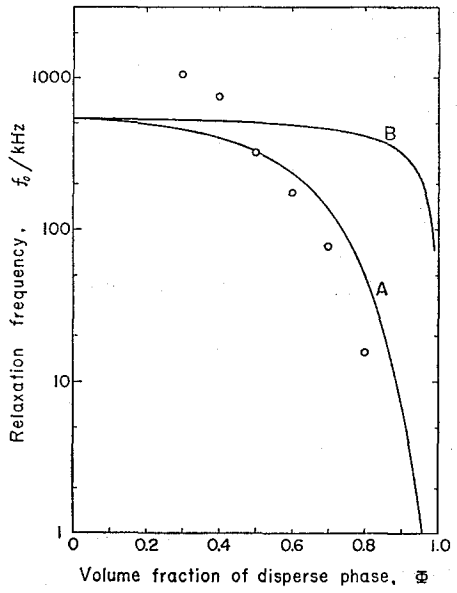

Fig. 3. Concentration dependence of relaxation frequency f_0 calculated from Equation (4) (Curve A) and from Wagner's Equation (20) (Curve B). Values of the phase parameters used for the calculation are shown in Table I. The circles in the figure are the experimental data cited from the previous paper.[5)]

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